Soft X-ray spectromicroscopy studies of industrial polymers

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INTRODUCTION

Soft X-ray spectromicroscopy, using the ALS BL 7.0.1 scanning transmission X-ray microscope (STXM) offers many unique opportunities for chemical micro-analysis of materials of industrial relevance. Over the past year we have made significant progress in several areas, including quantitative speciation of mixed phases and analyses of artificial thin film structures. These capabilities are illustrated with results from studies of polyurethanes (Dow) and photoconducting films (Xerox). Unless indicated otherwise, all data was recorded at the ALS.

POLYURETHANES – QUANTITATIVE CHEMICAL ANALYSIS (SPECIATION)

Polyurethane polymers, in the form of free-rise or molded foams, are widely used in the automotive and furnishings industries. World-wide polyurethanes is a $2 billion business, of which Dow Chemical is a market leader. Quantitative, spatially resolved analysis of functional group composition (particularly the urea and urethane content) is needed to help understand the chemical basis for the microstructure of polyurethane polymers [1] and to correlate with physical and mechanical properties. We have demonstrated the quantitative analysis capabilities of NEXAFS spectromicroscopy [2] through a study of three test polyurethane polymers in which a controlled variation of the urea and urethane content was achieved by careful adjustment of the water content in the formulation. The C 1s, N 1s and O 1s edges were all investigated for their analytical potential; the C 1s spectrum was found to be most suited for quantitative analysis. **Fig. 1** illustrates the fit of the C 1s spectrum of one of these three standard species to the optimized sum of reference spectra [3].

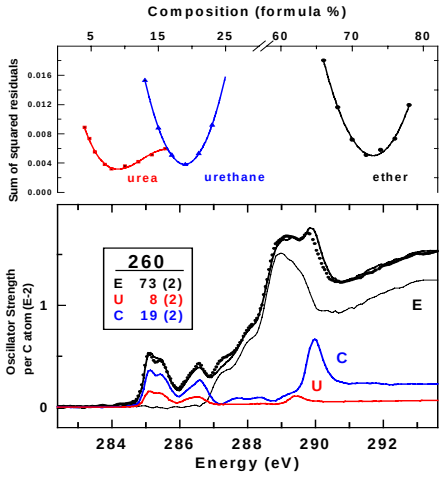

Fig. 1 Quantitative analysis of a urethane (carbamate)-rich polyurethane [2]. E=ether, U=urea, C=carbamate. Bottom: comparison of spectrum (dots) with optimized sum (lines). Top: compositional variation of residuals with ratio of other two components fixed. The fit is sensitive to few % changes in composition.

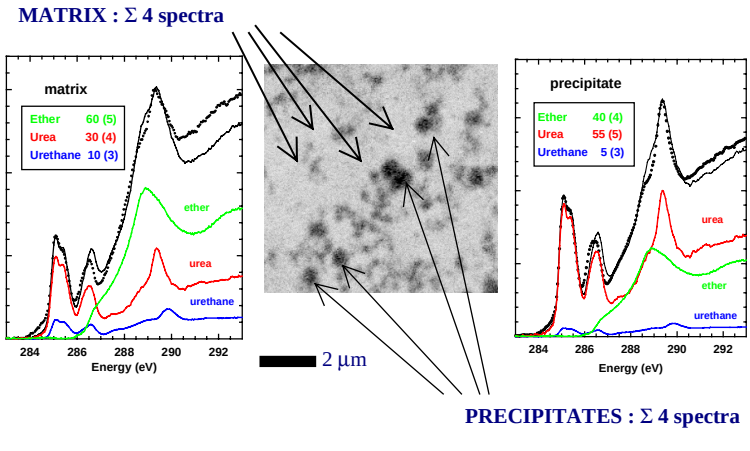

Fig. 2 Quantitative composition of matrix and precipitates based on fitting spectra [3]. This analysis was the first direct confirmation that precipitates in water-blown polyurethane foams are driven by urea insolubility in the reaction. (this data was recorded in point spectral mode at the Stony Brook STXM at NSLS)

Comparison with predictions from formulation chemistry indicates that C 1s NEXAFS can determine the content of chemical components at the 4-20 mol% level, with 10-20% accuracy. This is a remarkably good level of quantitation given the relatively small spectral differences which are the basis for this quantitative chemical analysis (mainly a shift of ~0.4 eV between the urea and urethane $\pi^*_{C=O}$ signals around 290 eV), and the extensive overlap of these key features with broad underlying σ^* resonances. The good energy resolution provided by the ALS BL 7.0 STXM (~0.1 eV) is very beneficial in being able to track the subtle changes in the line shapes in the 288-291 eV range which provide the sensitivity to quantitative composition.

Fig. 2 illustrates application of this analysis to a 'real world', macro-phase segregated poly-urethane [4] (for the test samples every effort was made to avoid heterogeneity). As illustrated, it is possible to obtain quantitative analysis near the limits of the spatial resolution. The image and spectra in Fig 2 were recorded with the Stony Brook STXM at NSLS, which has lower beam intensity but faster point spectral acquisition than the ALS. In order to obtain similar data at the ALS a 'stack' or 'linescan' approach is required. These methods are now being used routinely to obtain reliable, high spatial resolution analysis of radiation sensitive samples.

POLYURETHANES – CO-POLYOL POLYMER (CPP) PARTICLES

In order to make foams with higher hardness several different strategies are presently employed [5]. Copolymer polyols (CPP) – polymer dispersions in polyether polyol, inorganic fillers, and low molecular weight cross-linker polyols are preferred for stiffening slabstock foams. In order to understand how these co-polymer polyols affect mechanical properties such as elastic modulus, tear strength and resiliency, and in order to develop improved CPP substances, it is important to have analytical techniques which can probe the chemistry at the required spatial scale. While traditional chemical spectroscopies such as infrared or NMR are excellent at chemical speciation, they do not have adequate spatial resolution to address questions relating to the submicron composition of blends containing CPPs. Analytical transmission or scanning electron microscopy has superb spatial resolution but in many cases the high energy electron beam causes extensive radiation damage in fully focussed mode. In addition the chemical sensitivity of NEXAFS is better than electron energy loss spectroscopy on account of higher energy resolution.

STXM images at selected photon energies allow unambiguous identification of styrene-acrylonitrile (SAN)-based and poly-isocyanate poly-addition product (PIPA)-based particles down to particle sizes at the limits of STXM spatial resolution (50 nm) (**Fig. 3**) [6]. Surprisingly, the particle size distribution derived from the STXM images extends to smaller particle sizes than that from a TEM image [6]. This suggests that, in selected cases, X-ray microscopy may have advantages over electron microscopy even in primarily imaging applications, owing to superior chemical contrast mechanisms. A further aspect of the CPP study is the determination of the composition of individual SAN-CPP particles by fitting to sums of the component polymer spectra (pS, pAN). A number of particles were analyzed to study compositional distributions [6].

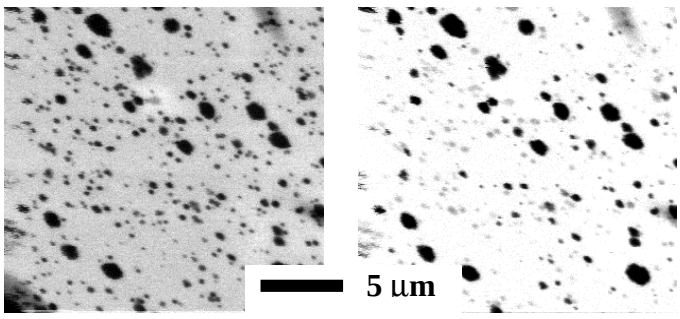

Figure 3. STXM images of a polyurethane made with both SAN and PIPA copolymer polyol (CPP) fillers. Both types of CPP are at high contrast in the left image (**285 eV**) whereas only the SAN is high contrast in the right image (**287 eV**).

ANALYSIS OF PHOTOCONDUCTING IMAGING FILMS

Polycarbonate (PC) capping layers are used to protect the photosensitive layer used to convert the image to charge in the xerographic process. The PC cap layers are doped with compounds which allow transfer of charge from the photosensitive layer to the outer surface, where the toner particles are deposited, patterned via electrostatic attraction, and ultimately transferred and fixed to paper. The ALS STXM has been used to investigate the spatial distribution of the charge transfer compound in an experimental xerography film. **Fig. 4** shows a STXM image of the film made in the N 1s energy region. Intensity profiles extracted from this image or linescans (**Fig. 5**) indicate a high degree of spatial uniformity of the charge transfer compound. N 1s spectra extracted from linescans across the film, showed that N 1s NEXAFS could readily distinguish the chemical form of the imaging agent and the charge transfer compound, and thus investigate the uniformity of contact between these two species, a critical aspect to the performance of the xerographic film.

Subsequent to the ALS STXM measurements, a complementary analysis was made of the same sample (same grid) using the McMaster high performance JEOL-2010F TEM/STEM equipped with a windowless X-ray fluorescence (EDS) detector, and pEELS. While the spatial resolution of the TEM images was significantly higher than STXM, the analytical information was inadequate to address the problem. In particular, pEELS did not see the nitrogen edge, and the N elemental map from EDS with ~70 minutes integration was insufficient to conclude anything about spatial uniformity, and gave no chemical speciation information (see **Fig. 6**).

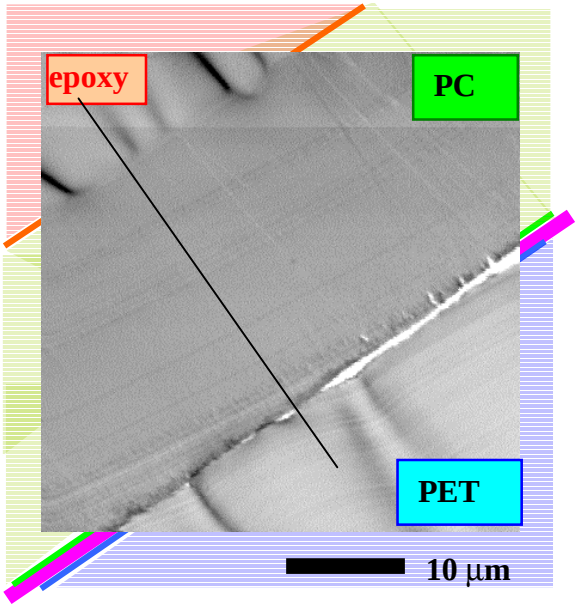

Fig. 4 Image at 410 eV of a cross-section of a photoconducting film embedded in epoxy. The optically active layer is at the PC-PET boundary. The analysis focussed on the degree of uniformity of a N-containing charge transfer agent in the polycarbonate (PC) cap layer . The line indicates the position of the linescan displayed in the next figure.

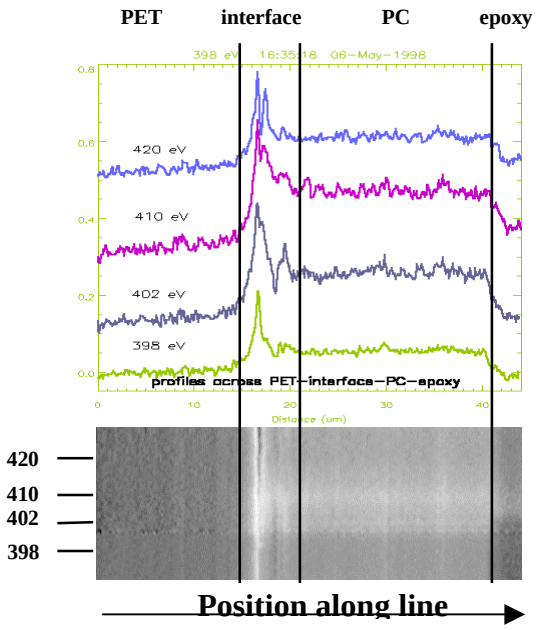

Fig. 5 Optical density profiles at different photon energies in the N 1s region extracted from a linescan across the PC layer of the photoconducting film. Aside from the irregular particles of the optically active component, the N-content in the PC layer is uniform to ~5%.

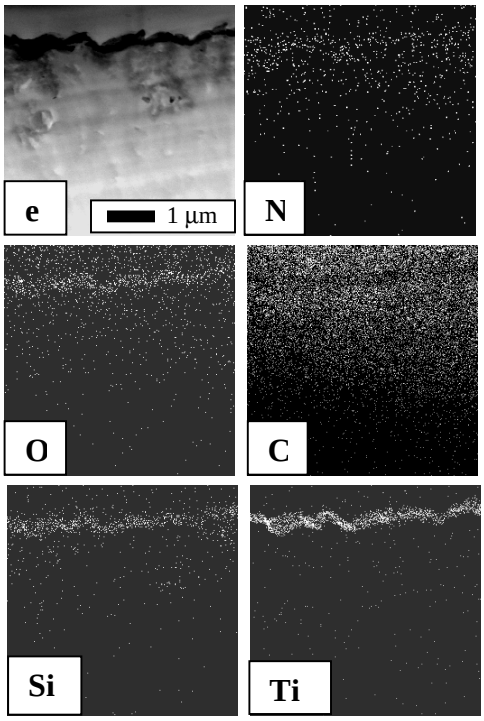

Fig. 6 Bright field and X-ray fluorescence (EDS) images (windowless detector) of the photoconducting film recorded using a JEOL 2010 scanning transmission electron microscope. Only a small amount of N in the region of the optically active layer was detected. In the N image each dot represents 1-5 counts. The image size was (256x256) with a total record time of 70 minutes (McMaster, May 1998).

SUMMARY

These examples clearly demonstrate the power of NEXAFS spectromicroscopy for studies of the chemical basis of sub-micron structure. The technique is particularly useful for quantitative analysis of radiation sensitive materials or systems which require subtle chemical differentiation, such as the urea-urethane distinction in polyurethanes. An additional attractive aspect is the ready ability to adapt STXM to a wide variety of environments, including studies of polymer and other particles in an aqueous environment (see presentation of hydrated super-absorbent polymers elsewhere in this compendium).

ACKNOWLEDGEMENTS

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